

3 / PRTS

10/501759

DT15 Res'd PCT/PTO 11/16 JUL 2004
PCT/GB03/00169

WO 03/063278

FUEL CELL OXYGEN REMOVAL AND PRE-CONDITIONING SYSTEM

The present invention relates to fuel cells, and in particular to methods and
5 apparatus for controllably removing oxidants in a fuel cell fuel supply
stream.

Conventional electrochemical fuel cells convert fuel and oxidant into
electrical energy and a reaction product. A typical layout of a conventional
10 fuel cell 10 is shown in figure 1 which, for clarity, illustrates the various
layers in exploded form. A solid polymer ion transfer membrane 11 is
sandwiched between an anode 12 and a cathode 13. The polymer membrane
allows protons to traverse the membrane, but blocks the passage of
electrons. Typically, the anode 12 and the cathode 13 are both formed from
15 an electrically conductive, porous material such as porous carbon, to which
small particles of platinum and/or other precious metal catalyst are bonded.
The anode 12 and cathode 13 are often bonded directly to the respective
adjacent surfaces of the membrane 11. This combination is commonly
referred to as the membrane-electrode assembly, or MEA.

20

Sandwiching the polymer membrane and porous electrode layers is an anode
fluid flow field plate 14 and a cathode fluid flow field plate 15. The fluid
flow field plates 14, 15 are formed from an electrically conductive, non-
porous material by which electrical contact can be made to the respective
25 anode electrode 12 or cathode electrode 13. At the same time, the fluid flow
field plates must enable the delivery and/or exhaust of fluid fuel, oxidant
and/or reaction products (and/or other diluent gases not taking part in the
reaction) to or from the porous electrodes. This is conventionally effected
by forming fluid flow passages in a surface of the fluid flow field plates,

WO 03/063278

PCT/GB03/00169

such as grooves or channels 16 in the surface presented to the porous electrodes.

Figure 2 shows a plan view of a typical fluid flow channel 16 arranged as a
5 serpentine structure 20 in a face of the anode 14 (or cathode) having an inlet manifold 21 and an outlet manifold 22. Many different configurations of fluid flow channel may be used.

In a typical application, in the anode fluid flow field plate 14, hydrogen gas
10 is delivered into the serpentine channel 20 from the inlet manifold 21. In the cathode fluid flow field plate 15, oxidant (eg. oxygen gas) is delivered into the serpentine channel 20 from the inlet manifold.

Prior to the start up of a fuel cell 10 after first assembly, commissioning,
15 repair, prolonged periods of inactivity or stand-by there can be an accumulation of air in the fuel flow channels and fuel delivery conduits, ie. generally within the fuel delivery path of the fuel cell. There is therefore a need to remove this air, or more particularly to remove the oxygen in the air, from the anode fuel delivery path before the introduction of any hydrogen
20 fuel or a hydrogen rich gas mixture to the anode 12 and membrane 11.

This removal of oxygen prior to delivery of fuel is important to prevent undesirable uncontrolled catalytic combustion occurring at the surface of the
25 anode 14 resulting in localized heating, dehydration and possible puncture of the proton exchange membrane 11.

In the prior art, it is common practice to purge the anode channels 16 and other portions of the fuel delivery conduits by passage of an inert gas, such as nitrogen, for a period of time prior to introduction of hydrogen fuel.

30

WO 03/063278

PCT/GB03/00169

This process necessitates a local supply of nitrogen, generally contained in a pressure cylinder, and its periodic replacement. It is desirable to eliminate this requirement and thereby simplify the operational and service needs of the system. This is particularly important when the fuel cell is already
5 installed in the field, eg. as part of a power system in a vehicle where accessibility of a purge gas, and indeed accessibility to the fuel cell, may be limited.

It is an object of the present invention to provide a convenient method and
10 apparatus for the removal of oxygen from the fuel delivery conduits of an electrochemical fuel cell.

It is a further object of the present invention to provide an apparatus by which the removal of oxygen from the fuel delivery conduits of an
15 electrochemical fuel cell may be effected automatically.

A further problem associated with start up of fuel cells is that the membrane-electrode assembly generally operates with optimum performance only once it has reached an ideal operating temperature and an ideal degree of
20 hydration of the membrane. Conventionally, such an optimum performance level is not achieved until after a period of operation of the fuel cell.

It is a further object of the invention to provide an apparatus by which a fuel and/or oxidant gas stream is pre-conditioned to accelerate hydration of the
25 membrane-electrode assembly and/or to accelerate heating of the membrane-electrode assembly towards an optimum operating condition.

According to one aspect, the present invention provides a fuel cell including an anode, a cathode, and an ion exchange membrane therebetween, and
30 having a fuel delivery conduit for supplying fuel from a fuel source to an

WO 03/063278

PCT/GB03/00169

active surface area of the anode and further comprising means for effecting a controlled combustion of fuel and oxidant species within the fuel delivery conduit.

- 5 According to a further aspect, the present invention provides a fuel cell system including:

a fuel cell having an anode, a cathode, and an ion exchange membrane therebetween;

a fuel delivery conduit comprising:

- 10 a fluid flow field plate forming part of the anode, having a fluid flow channel extending therethrough;

a fuel delivery inlet coupled to one end of the fluid flow channel; and

- 15 a fuel delivery outlet coupled another end of the fluid flow channel;

the fuel cell system further comprising

a recirculation conduit extending between the fuel delivery outlet and a mixing point in the fuel delivery inlet.

- 20 According to a further aspect, the present invention provides a fuel cell system including:

a fuel cell having an anode, a cathode, and an ion exchange membrane therebetween;

- 25 a fuel delivery conduit for delivering preconditioned fuel to the anode comprising:

a reaction chamber for reacting fuel and oxidant;

a fuel supply inlet for delivering fuel to the reaction chamber;

an oxidant supply inlet for supplying oxidant to the reaction chamber; and

- 30 a reaction chamber outlet connected to the anode;

WO 03/063278

PCT/GB03/00169

the reaction chamber being adapted so that at least a part of the fuel supply delivered thereto to is reacted with the oxidant supplied thereto to precondition the fuel being delivered to the anode.

5 According to a further aspect, the present invention provides a fuel cell system including:

a fuel cell having an anode, a cathode, and an ion exchange membrane therebetween;

an oxidant delivery conduit for delivering preconditioned oxidant to
10 the cathode comprising:

a reaction chamber for reacting fuel and oxidant;

a fuel supply inlet for delivering fuel to the reaction chamber;

an oxidant supply inlet for supplying oxidant to the reaction chamber; and

15 a reaction chamber outlet connected to the cathode;

the reaction chamber being adapted so that at least a part of the oxidant supply delivered thereto to is reacted with the fuel supplied thereto to precondition the oxidant being delivered to the cathode.

20 According to a further aspect, the present invention provides a method of operating a fuel cell having an anode, a cathode, and an ion exchange membrane therebetween, comprising the steps of:

supplying fuel from a fuel source to an active surface area of the anode by way of a fuel delivery conduit; and

25 effecting a controlled combustion of fuel and oxidant species within the fuel delivery conduit.

According to a further aspect, the present invention provides a method of operating a fuel cell having an anode, a cathode, and an ion exchange
30 membrane therebetween, comprising the steps of:

WO 03/063278

PCT/GB03/00169

supplying fuel from a fuel source to an active surface area of the anode by way of a fuel delivery conduit; and

reacting fuel and oxidant in a reaction chamber upstream of the anode to precondition the fuel being delivered to the anode.

5

Embodiments of the present invention will now be described by way of example and with reference to the accompanying drawings in which:

Figure 1 is an exploded cross-sectional view of a prior art fuel cell;

Figure 2 is a plan view of a fluid flow field plate in the fuel cell of figure 1;

Figure 3 is a schematic diagram of a first arrangement of an oxygen removal system according to the present invention;

Figure 4 is a schematic diagram of a second arrangement of an oxygen removal system according to the present invention;

Figure 5 is a schematic diagram of a preconditioning system for controlled combustion of fuel and oxidant in a fuel delivery conduit according to the present invention; and

Figure 6 is a schematic diagram of a further preconditioning system for controlled combustion of fuel and oxidant in a fuel delivery conduit according to the present invention.

25

One method of achieving oxygen removal from the fuel delivery path is to utilize the oxygen in a controlled catalytic combustion of hydrogen external to the fuel cell.

With reference to figure 3, a fuel cell 10 is coupled to fuel delivery conduits 30, 31 and oxidant / exhaust conduits 32, 33. The fuel delivery conduits 30, 31 respectively provide an inlet 30 and outlet 31 for delivery to and from the anode fluid flow field plate 14 (figure 1) while the oxidant supply conduit 32 provides a supply of the oxidant to an inlet end of the cathode fluid flow

WO 03/063278

PCT/GB03/00169

field plate 15 and the exhaust conduit 33 provides an outlet to exhaust unused oxidant and reaction products from the cathode.

5 A fuel supply (eg. hydrogen) is coupled to a system inlet 34 which is fed to a reaction chamber 35. A recycle loop 36 extends between outlet 31 and the reaction chamber. The recycle loop 36 incorporates a pump 37 and can be switched into operation using a two way valve 38.

10 The reaction chamber 35 contains a suitable catalytic material dispersed on a support, to enable the removal of oxidants passing therethrough, according to techniques well known in the art. Presently preferred catalytic materials include precious metals such as platinum or platinum alloys dispersed on a ceramic support such as alumina.

15 In a normal mode of use, a hydrogen fuel supply is provided to the fuel cell 10 by way of system inlet 34, preferably via a flow regulator or metering valve 39. The hydrogen fuel passes into the inlet manifold 21 and anode fluid flow field plate 14 (figure 1) where it is at least partially consumed. Any unconsumed fuel or inert diluent fluid in the fuel supply may be
20 exhausted via a fuel system outlet 22, when the two way valve 38 is switched to an exhaust position.

When the anode (fuel) stream is determined to be contaminated, or when it is suspected to be contaminated, by oxidant fluid, the system is switched to a
25 recirculation mode of use. In this configuration, the two way valve 38 is switched so that the fuel cell outlet 31 is connected to the recycle loop 36. If necessary to maintain fluid circulation, the recycle pump 37 is switched on. In this manner, the anode fluid stream is recirculated, passing through reaction chamber 35 where oxidant species are scrubbed from the fluid

WO 03/063278

PCT/GB03/00169

stream, preferably by reaction with a controlled bleed of hydrogen gas from fuel system inlet 34 and flow regulator 39.

In this manner, combustion of hydrogen and oxidant species is effected only
5 in the reaction chamber 35 and not in the fuel cell 10.

The recirculation mode of use may be initiated according to any desired prevailing condition. These conditions may include any one or more of the following: (i) automatic detection of oxidant in the fuel delivery conduit
10 inlet 30 and/or outlet 31 by means of an appropriate sensor mechanism (to be described later); (ii) automatic detection of a period of non-use of the fuel cell exceeding a predetermined elapsed time threshold; (iii) automatic detection of a period of use of the fuel cell exceeding a predetermined elapsed time threshold; (iv) automatic detection of a service condition, ie.
15 after detection of a fuel cell maintenance condition; and (v) manual initiation, by a user.

During the recirculation mode, the gases in the fuel cell can be recirculated around the recycle loop 36 and through the reaction chamber 35 into which
20 the hydrogen gas is being introduced in a controlled manner, until all of the unwanted oxygen is eliminated. This recirculation mode may continue automatically for a predetermined period of time, or may be continued automatically until detection of reduction of unwanted oxidant species to below a predetermined threshold. Alternatively, the duration of the
25 recirculation mode may be controlled manually by the user.

The metered supply of hydrogen fuel from the flow regulator 39 ensures that combustion of the fuel and oxidant is restricted to the volume of the reaction chamber 35 and that no combustion takes place within the fuel cell itself.

30

WO 03/063278

PCT/GB03/00169

The presence of an oxidant species in the fuel delivery conduits and in the anode conduits may be detected by a number of methods. A low, near zero, open circuit voltage of the fuel cell stack 10 is often a good indicator of the presence of oxygen on the anode electrode face. Once this oxygen has been substantially removed, then the hydrogen will break through the reaction bed and transfer to the fuel cell anode surface thereby elevating the open circuit voltage and indicating successful oxygen elimination.

Thus, in one presently preferred embodiment, prior to operation of the fuel cell, the open circuit voltage is tested. If this open circuit voltage is lower than a predetermined threshold, the system determines that a recirculation mode of operation using a low flow hydrogen supply should be initiated prior to entering normal operating mode. In a further embodiment, the open circuit voltage is continuously monitored during the recirculation mode until the open circuit voltage exceeds a predetermined threshold.

In a further embodiment, the oxygen level may be detected by monitoring the temperature of the reaction chamber, or outlet thereof, using an appropriate thermocouple or thermistor. During the period when oxygen is being reacted with fuel in the reaction chamber, the temperature of the reaction chamber, or of the gas flow exiting the reaction chamber, will continue to rise. Once the temperature rise ceases, begins to fall or slows below a predetermined rate of increase, it can be determined that the oxygen level has reduced to below an appropriate threshold indicating that the fuel cell may be brought into normal operating mode.

Once the oxygen has been removed, the hydrogen flow rates can be increased to such levels as are consistent with normal power delivery from the fuel cell and normal operation can begin.

30

WO 03/063278

PCT/GB03/00169

With reference to figure 4, an alternative method of achieving oxygen removal from the fuel delivery path is to utilize the oxygen in a controlled combustion of hydrogen internally of the fuel cell.

- 5 In this embodiment, the reaction chamber 35 is removed and the recycle loop 36 delivers the recirculated gas stream to a mixing point 40 where it is mixed with the controlled low flow bleed of hydrogen fuel from fuel system inlet 34 and flow regulator 39.
- 10 Preferably, the mixing point 40 comprises a pre-mixing chamber 41 incorporating a plurality of mixing baffles or other suitable physical structure to encourage a thorough mixing of fuel fluid with recirculation fluid prior to entry into the fuel cell. In this manner, a very controlled, low level reaction can be effected at the anode of the fuel cell in such a manner
- 15 as to avoid any significant level of damage to the fuel cell.

This relies on the catalytic activity at the anode surface in the fuel cell 10 to promote the reaction of fuel and oxidant in situ. Provided that close control of hydrogen dosing is observed and good pre-mixing before entry into the

20 fuel cell occurs, then localized heating effects within the anode will be avoided and good reaction distribution will occur avoiding damage to the fuel cell.

The metered hydrogen fuel may comprise a hydrogen rich gas, for example,

25 a hydrogen and inert diluent fluid mixture, offering further improvement in fuel and oxidant mixing.

Similar to the embodiment of figure 3, automatic control means may be provided for determining when the recirculation mode is to be initiated, and

30 for how long, prior to switching to a normal mode of operation.

WO 03/063278

PCT/GB03/00169

A further aspect of preventing or limiting damage to the membrane-electrode assembly is to ensure that fuel delivered to the anode is provided at an optimum temperature and/or humidity. During a start up phase, control
5 of the temperature and/or humidity of the fuel stream can also accelerate the process of achieving an optimum operating condition in the fuel cell.

With reference now to figure 5, an adaptation of the process described in connection with figure 3 can be made to pre-condition the fuel flow by
10 introducing water or steam to improve or maintain humidity in the fuel gas stream. A further benefit of this arrangement is that the temperature of the fuel stream can also be controlled.

To achieve this fuel pre-conditioning, provision is made to deliver oxidant
15 (eg. air) into the reaction chamber 35 to deliberately increase the reaction of hydrogen with oxygen for the purpose of producing water and heat.

An oxidant supply line 50 is connected to supply of suitable oxidant. In the preferred embodiment shown, this supply is conveniently the same source of
20 oxidant used to supply the cathode, namely the oxidant supply conduit 32. The oxidant supply line 50 is coupled thereto by a valve 51, which may also incorporate a flow regulator (not shown separately). This system configuration may be used with or without the recycle loop 36 depicted in figures 3 and 4.

25

The provision of controlled quantities of oxidant to the reaction chamber 35 results in a predetermined rate of reaction of hydrogen and oxygen in the reaction chamber, thereby enabling control of the temperature and humidity of the fuel gas being fed to the fuel cell 10 anode via fuel delivery conduit

WO 03/063278

PCT/GB03/00169

inlet 30 (assuming, of course, that the fuel supply from flow regulator 39 provides excess fuel to that required by the oxidant supply).

5 The flow of water or water vapour to the fuel cell 10 (and its continued re-circulation if used in combination with the recycle loop 36) allows the hydration state of the membrane to be controlled hence maintaining conductivity by use of a pre-conditioned fuel stream.

10 This facility is particularly useful in the operation of fuel cells of open cathode design, which are prone to membrane dehydration when not operated for extended periods of time.

15 Energy is liberated in the course of the reaction in reaction chamber 35 and therefore offers the opportunity to deliver heat directly to the fuel cell or any other part of the associated system by means of heat exchange / transfer mechanisms. This may be of particular use when starting a fuel cell from cold where the rapid elevation of temperature will ensure a shorter time to normal operational temperature and maximum power capability.

20 In any case the use of a catalytic reactor, upstream of fuel gas introduction and /or in a recirculation loop provides the additional flexibility of controlling fuel gas humidity and introducing heat via the gas stream.

25 With reference to figure 6, a further arrangement is shown that allows for provision of humidification and pre-heating of both the fuel flow to the anode of the fuel cell 10, and separate humidification and pre-heating of oxidant flow to the cathode of the fuel cell 10.

30 In this arrangement, the fuel system inlet 34 is coupled to feed a first reaction chamber 35 within the fuel delivery conduit 30, which is supplied

WO 03/063278

PCT/GB03/00169

by an oxidant supply line 50. The oxidant supply conduit 32 incorporates a second reaction chamber 60 which is supplied by a fuel supply line 61. Appropriate valves 62, 63 control the flow of oxidant and fuel to respective first and second reaction chambers 35, 60, which valves may also include
5 flow regulators for varying flow rate according to a desired degree of humidification and/or pre-heat.

It will be understood that either or both of the first and second reaction chambers could be used independently of the other. In addition, the system
10 of figure 6 could also be used in conjunction with a recycle loop as described in connection with figure 3.

The preconditioning mode of operation described in connection with figures 5 and 6 may be initiated according to any desired prevailing condition.
15 These conditions may include any one or more of the following: (i) automatic detection of a period of non-use of the fuel cell exceeding a predetermined elapsed time threshold; (ii) automatic detection of a period of use of the fuel cell exceeding a predetermined elapsed time threshold; (iii) automatic detection of a service condition, ie. after detection of a fuel cell
20 maintenance condition; (iv) automatic detection of a predetermined temperature or humidity condition in the fuel delivery conduit or fuel cell, and (v) manual initiation, by a user.

The preconditioning mode of operation may continue automatically for a
25 predetermined period of time, indefinitely, or may be continued automatically until detection of a suitable temperature or humidity condition in the fuel delivery conduit or fuel cell. Alternatively, the duration of the preconditioning mode may be controlled manually by the user.

WO 03/063278

PCT/GB03/00169

Throughout the present specification, for convenience the fuel cell 10 has been described in terms of only a single anode, membrane and cathode. However, it will be understood that, in accordance with conventional fuel cell design, multiple membrane-electrode assemblies are used in series or in parallel in a stack in order to increase the voltage and/or current supply. In accordance therewith, the fuel delivery conduit typically incorporates a plurality of anode fluid flow field plates, and the oxidant supply conduit typically incorporates a plurality of cathode fluid flow field plates. The principles of the present invention apply equally to such membrane-electrode assembly stacks.

The invention has been described with reference to a conventional MEA comprising a polymer membrane, but is also relevant to other types of fuel cell.

Other embodiments are within the accompanying claims.